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CROSS-LINKABLE AND/OR CROSS-LINKED NANOFILLER COMPOSITIONS

FIELD OF THE INVENTION

The present invention relates to cross-linkable and/or cross-linked nanofiller compositions, processes for their preparation and articles composed of them, in particular cross-linkable and/or cross-linked nanofiller compositions containing cross-linkable and/or cross-linked ethylene (co)polymers such as polyethylene. These nanofiller compositions possess advantageous properties, more specifically, increased barrier properties, strength and higher heat distortion temperatures which makes them useful in various applications including medical, automotive, electrical, construction and food applications.

BACKGROUND OF THE INVENTION

Thermoplastic polymers such as thermoplastic polypropylene have been mixed with fillers such as clays or calcium carbonate to produce compositions which only show minimal improvement in mechanical and chemical properties with deterioration during processing.

When nanofillers were added to thermoplastic polymers such as polypropylene in reduced amounts compared to standard fillers, some improvements in properties were obtained such as increased mechanical properties including stress crack resistance and tensile strength, reduction in gas or liquid permeability and increases in crystalline melting temperatures and flame retardancy e.g. reduced dripping in a flame. However, despite the addition of nanofillers, thermoplastic polymers such as polypropylene are still thermoplastic and their thermo-mechanical properties, tensile strength, resistance to permeability of gases or liquids, resistance to swelling and solvents and flame retardance at higher temperatures including in heat and sunshine is still reduced or limited. This is even more the case with polyethylene which has much lower

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crystalline melting temperatures than polypropylene.

Polyethylene is not traditionally treated in this way because of difficulties in achieving even limited improvements in the above mentioned properties and in

5 general these problems are considered as not being solved with polyethylenes or ethylene copolymers.

The Stress Crack Resistance (SCR) and Environmental Stress Crack Resistance (ESCR) of most thermoplastics at greater than ambient temperatures such 10 as in cars and cables can still be weakened, insufficient and can fail both in prolonged tests and use, in particular in the presence of chemicals, detergents, solvents, liquid fuels and oils.

The swellability and solubility of polyolefin 15 thermoplastics e.g. ethylene polymers in certain solvents, fuels, oils, chemicals strongly increases at elevated temperatures up to unacceptable limits and they may dissolve at elevated temperatures or when boiled or extracted in solvents at higher temperatures.

20 Swellability means deterioration in properties, softening, increase in dimensions, mechanical weakening to the point of structural failure of the product made therefrom and ultimately, in some cases to dissolution of the product.

The flame retardance e.g. of a thermoplastic 25 polymer that has already flame retardant additives, in case of a test or in a real fire, can be reduced or impaired by the dripping thermoplastic polymer in particular in the flame temperature ranges. Dripping can result in acceleration of the fire due to hot, molten, 30 even burning drops of polymer falling on other parts of products under or in the vicinity of the burning polymer.

Thus, the improvements observed by the addition of nanofillers to thermoplastic polymers were not and are not sufficient to reach the higher levels of performance 35 required for increased safety levels of the products made therefrom both mechanically and thermo-mechanically, in particular at higher temperatures or in other difficult

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conditions such as exposure to chemicals, solvents, oils, fuels or short circuits. These properties are very important for products such as fuel tanks for automobiles, containers for solvents, chemicals, cables, aerial cables, 5 power cables, foils and films. Furthermore, such compositions cannot be used to make heat shrinkable products for joints, sleeves, tubes, pipes, films and packaging.

A requirement accordingly exists for a 10 nanofiller composition or nanocomposite containing thermoplastic polymers which has improved properties so that the products made from these compositions perform well, particularly at temperatures above ambient and/or in difficult environments such as exposure to chemicals, 15 solvents, oils, fuels or short circuits.

SUMMARY OF THE INVENTION

The present invention provides a cross-linkable and/or cross-linked nanofiller composition which comprises 20 a cross-linkable and/or cross-linked ethylene (co)polymer and an intercalated nanofiller.

Preferably, the composition further comprises an organic silane grafted to the ethylene (co)polymer and/or intercalated into the nanofiller.

25 The present invention also provides a process for preparing a cross-linkable and/or cross-linked nanofiller composition which comprises either:

(a) mixing and exfoliating and/or delaminating in one step a cross-linkable ethylene (co)polymer and an 30 intercalated nanofiller;

(b) mixing a cross-linkable ethylene (co)polymer with an intercalated nanofiller; and delaminating and/or exfoliating at least part of the nanofiller; or

35 (c) delaminating and/or exfoliating at least part of an intercalated nanofiller; and mixing the delaminated and/or exfoliated

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intercalated nanofiller with a cross-linkable and/or grafted ethylene (co)polymer.

In another aspect of the process, the ethylene (co)polymer and/or nanofiller are subjected to grafting either before, during or after the mixing and delaminating and/or exfoliating step(s). The grafting preferably involves treating the ethylene (co)polymer and/or nanofiller with an organic silane which is then grafted onto the (co)polymer and/or intercalated into the nanofiller using a free radical initiator.

The present invention further provides an article which is wholly or partly composed of the nanofiller composition defined above.

In a further aspect, the present invention provides a process for preparing the article defined above which comprises either:

- (a) forming or shaping the nanofiller composition defined above;
- (b) combining at least one layer of the nanofiller composition with at least one other layer;
- (c) cross-linking the nanofiller composition defined above; or
- (d) heating and stretching the nanofiller composition defined above and cooling the stretched composition.

DETAILED DESCRIPTION OF THE INVENTION

Suitable ethylene (co)polymers include polyethylene and ethylene based alkene or alphaolefin copolymers, for example, high density polyethylene (HDPE), medium density polyethylene (MDPE), linear low density polyethylene (LLDPE), low density polyethylene (LDPE), very low density polyethylene (VLDPE), and ultra low density polyethylene (ULDPE); ethylene hexene copolymers and ethylene octene copolymers; butylene (co)polymers such as polybutylene and polyisobutylene; ethylene-propylene copolymers (EPM); ethylene-propylene-diene terpolymers

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- (EPDM); ethylene-butylene copolymers (EBM) and terpolymers (EBDM); ethylene-vinylsilane (co)polymers; copolymers or terpolymers of ethylene with acrylic acid (EA) or ethylene with ethylene acrylate and acrylic acid (EAA) or
- 5 methacrylic acid (EMA); and copolymers of ethylene with ethylacrylate (EEA), butyl-acrylate (EBA) or vinyl acetate (EVA). It will be appreciated that these ethylene (co)polymers may also be in the form of metallocene catalyst (co)polymers.
- 10 The ethylene (co)polymers or part of the ethylene (co)polymers may be grafted with compounds containing carboxylic acid or anhydride groups such as maleic anhydride or acid or fumaric anhydride or acid which may facilitate the exfoliation and/or delamination
- 15 of the nanofiller. Examples of grafted ethylene (co)polymers suitable for use in the present invention include maleic anhydride (MAH) or maleic acid grafted copolymers such as LDPE-MAH, HDPE-MAH, EP-MAH, EPR-MAH, PE-MAH or PP-MAH.
- 20 In a preferred embodiment, the ethylene (co)polymer contains or has added, for example, by grafting, polar groups, such as carboxylic groups, for example, EEA or EA, maleic groups or ester groups, for example, EVA, EEA or EBA.
- 25 The amount of (co)polymer with polar groups should preferably be at least about 0.01% of the total (co)polymer, more preferably at least about 0.5%, most preferably at least about 5% and even more preferably at least about 8%. In the case of premix
- 30 masterbatches/concentrates of nanofiller with (co)polymer(s) the amount of (co)polymer with polar groups is preferably at least about 10%, more preferably at least about 15%, most preferably at least about 25% of the (co)polymer in the masterbatch/concentrate.
- 35 The ethylene content of the ethylene-propylene copolymers is preferably about 10 to about 99.9% by weight, more preferably about 40 to about 99.9% by weight,

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most preferably about 75 to about 99.9% by weight. Unless stated otherwise, it will be understood that the term "% by weight" as used herein is based on the total weight of (co)polymer.

- 5 The vinyl acetate content of the ethylene-vinyl acetate copolymer (EVA) is preferably about 3 to about 80% by weight, more preferably about 9 to about 70% by weight. The vinyl acetate content is preferably about 9 to about 30% by weight for plastomeric EVA and about 38 to about 10 50% by weight for elastomeric EVA.

The ethylene (co)polymer may be an elastomer or a plastomer. Plastomers and elastomers can be characterised by means of specific gravity (S.G.) or density, for example, in the case of ethylene-alpha-olefin 15 copolymers and other properties such as the differential scanning calorimetry (DSC) melting peak, Shore A hardness and elasticity modulus. Such properties will vary depending on the type of ethylene (co)polymer and its method of manufacture and the amount of (co)monomer 20 present. By way of example, EVA with up to about 28% VA is considered a plastomer and with above about 38% being considered an elastomer. However, generally plastomers are plastomeric and elastomers are elastomeric or thermoplastic elastomeric and flexible.

- 25 Preferably, for plastomeric cross-linkable compositions, at least about 40% to about 50% by weight, more preferably at least about 60% by weight is a plastomer with the balance being an elastomer. Examples of plastomers include polyethylene such as HDPE, MDPE, 30 LDPE, LLDPE or VLDPE; EVA with up to about 30% vinyl acetate; EPM with up to about 25% propylene; and ethylene octane copolymers with S.G. up to about 0.886. The elastomers include ethylene octane copolymers with an S.G. of at least about 0.887; ULDPE; ethylene propylene 35 copolymers such as terpolymers with propylene co-monomers of greater than about 30%; ethylene vinyl acetate copolymers with greater than about 38% vinyl acetate;

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EPDM; EPM; and EPR. Preferably, for plastic-elastomeric or elastomeric cross-linkable compositions, the elastomeric component will be at least about 40%, preferably about 50%, more preferably at least about 60% 5 by weight of the total composition. The most preferred embodiment of this invention is a thermoplastic cross-linkable composition with at least about 40% plastomeric compound by weight of the total composition.

The term "cross-linkable and/or cross-linked" is 10 used herein in its broadest sense and refers to the ethylene (co)polymer and/or a composition based on it being cross-linked or at least capable of being cross-linked at a later stage or of being made cross-linkable. It will be understood that at least one ethylene 15 (co)polymer in the composition may be cross-linkable and/or cross-linked and such a (co)polymer preferably forms at least about 30%, more preferably about 50%, most preferably at least about 70% by weight of the total (co)polymer component.

20 The term "nanofiller" is used herein in its broadest sense and refers to fillers having a particle size in the nanometre (nm) range, in the order of size of less than about 500nm. The thickness of the particles is approximately in the order of about 1nm to about 100nm and 25 the diameter or length or width can be up to about 500nm. The ratio between thickness and length or width of the particles is called "aspect ratio" and it is preferred to have or to achieve a high aspect ratio. The particles have a platelet like structure. A nanofiller is capable 30 of being separated by intercalation, delamination and or exfoliation into smaller size groups or layers of less than 100 nanometres thickness, into particles or layers with 1 to no more 5 platelets, preferably into a high proportion of single platelets. When the nanofillers are 35 exfoliated, the thickness of their platelets is reduced to about 1 to about 3nm. The nanofiller may be present in an amount of about 15 to about 40%, preferably about 15 to

about 30% of the masterbatch/concentrate.

The term "intercalated" or "intercalation" is used herein in its broadest sense and refers to a platelet-like or layered structure. The layers of the
5 nanofiller which are generally composed of silicate are treated chemically by removing some cations from between the layers and intercalated with ionic or polar substances including quaternary ammonium salts, including quaternary ammonium salts, such as, optionally substituted long chain
10 hydrocarbon quaternary ammonium salts, for example, benzyl or alkyl substituted long chain hydrocarbon quaternary ammonium salts, alkyl substituted tallow or hydrogenated tallow quaternary ammonium salts; or bis-hydroxyethyl quaternary ammonium salts. Suitable counter anions for
15 the quaternary ammonium cations include halides such as chloride or methyl sulphate.

The intercalated nanofiller may be an intercalated mineral nanofiller or clay which is either synthetic or natural, such as, montmorillonite, bentonite,
20 smectite and phyllosilicate which can be or have been intercalated by organic modification with an organic intercalatent selected from the ionic or polar compounds described above and may be sold under the trade names Cloisite (Southern Clay Products), Nanofil (Sudchemie),
25 Tixogel (Sudchemie) and Kunipia.

The organic intercalatent may be present in an amount up to about 40% by weight of the nanofiller. The weights in the description and examples refer to the nanofiller as supplied including the organic
30 intercalatent.

It should be noted that in some instances the word "intercalation" includes the situation when intended to refer to nanofillers which have been intercalated with the organic intercalatent and the distance between their
35 platelets is increased by a few nanometres are mixed with (co)polymer(s) and the (co)polymer molecules enter between the nano platelet layers thus further intercalating them

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so that they are delaminated in the mixing process. This type of further intercalation is herein referred to as "delamination" and/or "further intercalation" / delamination / exfoliation. The step of delamination and 5 exfoliation is very important. The effects of this step can be seen in the changes and improvements in the mechanical and thermo-mechanical and chemical and optical and X-ray diffraction properties of the compositions.

Nanofillers such as montmorillonite have an 10 anisotropic, plate like, high aspect-ratio morphology which leads to a long and tortuous diffusion path through the structure and an improved barrier to permeation, particularly when used in combination with the cross-linked ethylene (co)polymers of the present invention.

15 The amount of nanofiller is about 0.1 to about 15%, preferably about 1 to about 10%, more preferably about 2 to about 6% by weight.

It will be appreciated that known fillers may 20 optionally and/or additionally be included in the composition. Suitable known fillers include inorganic and/or mineral fillers such as clays which may be calcined; talc; mica; kaolin; alkaline earth metal carbonates, for example, calcium carbonate, magnesium calcium carbonate or hydrated basic magnesium carbonate; 25 and metal hydroxides, for example, aluminum or magnesium hydroxide. The fillers may optionally be coated with, for example, stearic acid, stearates such as calcium stearate, silanes such as vinyl silane, siloxanes and/or organo-titanates. While such coatings can be used to coat the 30 fillers, they can also be added simultaneously, sequentially and/or separately with the fillers.

The composition of the present invention may be subjected to (i) silane grafting; (ii) the addition of cross-linking agents; and/or (iii) radiation cross-linking 35 at any step of the process.

(i) The silane grafting may be performed using an organic silane and a free radical initiator. In

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an embodiment preferred for economical reasons, effective amounts of organic silane and peroxide are added to the (co)polymer and/or nanofiller either before or during the mixing step and then grafted onto the (co)polymer at 5 temperatures preferably of about 160 to about 240°C, more preferably about 180 to about 230°C, most preferably about 190 to about 220°C. This grafting is carried out either in the first mixing step or in a subsequent or even in a separate mixing step, after the (co)polymer and nanofiller 10 have been mixed. In a particularly preferred embodiment, the silane and the peroxide are added to both the (co)polymer and/or nanofiller which facilitates exfoliation and/or delamination of the nanofiller and grafted to the polymer in one step. In an alternative 15 embodiment, the (co)polymer is grafted using the organic silane and peroxide and then mixed with the nanofiller followed by exfoliation and/or delamination.

In another embodiment, the (co)polymer(s), of which at least one has polar group(s), is or are mixed 20 with the nanofiller for the purpose of polymer intercalation and/or delamination or exfoliation at temperatures up to about 200°C. The resulting intercalated polymer is then mixed in a second step with further (co)polymer, a free radical initiator peroxide and an 25 organic silane and grafted onto the (co)polymer(s) at higher temperatures, preferably about 190 to about 220°C. The masterbatch of nanofiller in a (co)polymer(s) can be made with about 15 to about 45% nanofiller content. It is then subsequently mixed in a second step with further 30 (co)polymer(s) and then grafted with peroxide and vinyl silane in the same second step or in a third step.

Suitable organic silanes include vinyl silanes, for example, vinyl alkoxy silane such as vinyl-tris-methoxy-silane (VTMOS), vinyl-tris-methoxy-ethoxy-silane 35 (VTMOEOS), vinyl-tris-ethoxy-silane, vinyl-methyl-dimethoxy-silane and gamma-methacryl-oxypropyl-tris-methoxy-silane; or long aliphatic hydrocarbon chain

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silanes.

Vinyl silanes are preferred and may be added in an amount from about 0.5 to about 2.2% by weight of the (co)polymer, preferably about 0.8 to about 2%, more preferably about 1 to about 1.8% by weight.

The term "free radical initiator" is used herein in its broadest sense and refers to an unstable molecule or compound which generates free radicals. Examples of suitable initiators include peroxides such as dicumyl peroxide, di-tertiary-butyl peroxide, tertiary-butyl-cumyl peroxide and bis-tertiary-butyl-cumyl peroxide i.e., di(tert-butyl-peroxy-diisopropyl benzene) and 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane. The free radical initiator is preferably added in an amount of about 0.05 to about 0.3% by weight calculated on the amount of (co)polymer, more preferably about 0.15 to about 0.2% by weight. For this type of subsequent cross-linking the presence of moisture, water or steam is required, preferably with a catalyst added. A wider, more flexible range of ratios of peroxide to vinylsilane to be grafted is possible. The peroxide addition is possible up to about 0.5%.

Silane cross-linking is also called moisture cross-linking. After forming the article made by extrusion and/or moulding, film forming is carried out in the presence of water, steam or moisture at ambient or preferably at higher temperatures of up to about 90°C to about 100°C or higher if pressure is applied. Catalyst e.g. di-butyl-tin dilaurate (DBTDL), di-octyl-tin dilaurate (DOTDL), is added to the cross-linkable composition prior to or during forming, or it can be added to the water used for cross-linking in it as a medium.

The speed and the duration of the cross-linking will depend on the type of (co)polymer and nanofiller used in the composition, of the temperature, of the humidity or water present and of the thickness of the composition.

(ii) The (co)polymers, compositions and/or

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articles of the present invention may be cross-linked by adding cross-linking agents such as organic peroxides, for example, dicumylperoxide, di-tert-butyl peroxide, and/or di-tert-butyl cumyl peroxide preferably in amounts of

5 about 1.4 to about 2.2% by weight. These agents are added to the (co)polymer and nanofiller either by absorption at temperatures where they are or become liquid (e.g. at about 60°C), or in a subsequent melting process in a mixer keeping the temperature of the melt below the

10 decomposition temperature of the peroxide(s) i.e., below about 120°C. Silanes are not required in this process for grafting, however they may be added or have been added separately to the filler(s) or added in the mixing process prior to or during the mixing of the peroxide to the

15 (co)polymer and nanofiller mix preferably keeping below about 120°C. Co-agents such as polyallylcyanurates (TAC and Sartomer 350) may also be added prior to or during the mixing of the peroxide(s).

The composition can be cross-linked at

20 temperatures above the decomposition temperature of the peroxide(s) in the absence of oxygen. The cross-linking of the peroxide cross-linkable composition or the resulting products may be conducted after forming of the article by extrusion and/or moulding, in steam or nitrogen

25 or liquids such as molten salt mixtures, for example, potassium nitrate-nitrite mixtures under pressure at elevated temperatures, higher than the decomposition temperatures of the peroxides used to form free radicals at about 150 to about 220°C.

30 (iii) The radiation cross-linking may be conducted using gamma-radiation, for example, CO⁶⁰ or high energy electron beam radiation in air or under nitrogen at ambient or above ambient temperatures. Co-agents such as Sartomers, which enhance radiation cross-linking and

35 enable a lower radiation dose to be used, can also be added either during or subsequent to the mixing step preferably in an amount of about 1 to about 3% by weight.

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Examples of such co-agents include unsaturated allylic compounds, triallylcyanurate, acrylic compounds and acrylate or polyacrylate compounds. Protection against radiation damage to the (co)polymer can also be achieved 5 by the addition preferably of up to about 2% by weight of radiation protectors such as trimethyl quinoline polymers or oligomers, for example, Age Rite Resin D and Anox HB. The (co)polymer and/or composition may also be cross-linked after grafting the (co)polymer or composition with 10 an organic silane with the aid of a free radical initiator. Catalysts for cross-linking include DBTDL (di-butyl-tin-dilauroate) or dioctyl-tin-dilauroate (DOTDL) or other known catalysts.

Radiation cross-linking may be carried out at 15 room temperatures or rising above ambient due to the high energy radiation.

It will be appreciated that one or more additives known in the art of polymer processing can also be included in the composition and added at any stage of 20 the process. They can be added during the mixing steps or at the stage of forming in the form of masterbatches/concentrates incorporated separately or in the catalyst masterbatch. Suitable additives include antioxidants, for example, phenolic antioxidants such as 25 SANTONOX R marketed by Monsanto and IRGANOX 1010 which is pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate or IRGANOX 1035 which is octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, Irganox B900, or process stabilisers such as 30 Irgafos 168 marketed by Ciba-Geigy or aminic antioxidants such as Vulcanox HS and Flectol H which are polymerised 2,2,4-trimethyl-1,2-dihydroquinoline; metal deactivators and/or copper inhibitors, for example, hydrazides such as oxalic acid benzoyl hydrazide (OABH) or Irganox 1024 which 35 is 2,3-bis-((3-(3,5-di-tert-butyl-4-hydroxyphenyl)proponyl)propiono hydrazide; UV absorbers, for example Tinuvin or HALS type UV absorbers; foaming or blowing

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agents which may be either endothermic or exothermic for example, p,p-oxybis benzene-sulfonyl-hydrazide, azo-iso-butyro-nitrile and azodicarbonamide; processing and/or thermal stabilisers, for example tris (2,4-ditert-
5 butylphenyl) phosphite (phosphite based), pentaerythritol tetrakis (3-(3,5-di-tertbutyl-4-hydroxyphenyl)propionate), octadecyl-3(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 3,3',3',5,5',5'-hexa-tert-butyl-a,a',a'-(mesitylene-2,4,6-triyl)tri-p-cresol (phenolic based) and dioctadecyl-3,3'-
10 thiodipropionate (thioester based); pigments, for example, inorganic pigments such as titanium dioxide and carbon black and organic pigments; flame retardants, for example, borates and metaborates such as zinc borate or metaborate, glass beads or particles, silica, silicon dioxide,
15 compounds of silicon dioxide with other metal oxides; extenders, plasticisers or softeners, for example, polymeric plasticisers, phthalates such as dioctylphthalate, dioctylsebacate or dioctyladipate or mineral oils such as naphthenic, paraffinic or aromatic
20 oils.

The (co)polymers are preferably granulated, pelletised, powderised, cut and/or diced. The (co)polymer and the nanofiller can then be pre-mixed or added simultaneously, sequentially and/or separately to any suitable known apparatus, such as roll mills, internal mixers, for example, of the Banbury or Shaw type, single screw mixers of the Buss-Ko-Kneader type or continuous mixers, for example, twin screw mixers such as contra-rotating or co-rotating or co-rotating twin screw mixers
25 i.e., Werner Pfleiderer ZSK. It will also be understood that the known fillers and/or additives can be added simultaneously, sequentially and/or separately at any stage of the processing.

The nanofiller or composition may be
35 intercalated with (co)polymer(s), delaminated and/or exfoliated using any suitable known technique such as high shear processing, for example, in the mixing apparatus

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referred to above. In variations of process steps (a) to (c) defined above, a further exfoliation and/or delamination step may be performed using the mixing apparatus described above.

5 Similar mixing apparatus may be used for silane grafting (i) described above.

For mixing, delaminating, exfoliating and/or silane grafting, these mixing apparatus may be equipped with nitrogen blanket applicators, pre-dryers, either pre-mixing and/or dosage equipment/pumps for the silane and peroxide mix, side-feeders, vacuum ports, several entry ports, granulation, pelletising and/or dicing equipment.

10 Mixing is preferably performed in one step, for economical reasons. It can also be done in two separate
15 steps.

In one embodiment, the first step involves mixing and intercalation/delamination/exfoliation preferably at temperatures at up to about 200°C and then separately grafting the silane with peroxide in a second
20 step at temperatures of above about 200°C, but preferably not higher than about 220°C.

In another embodiment, the (co)polymer(s) are grafted in a first step at about 200°C to about 240°C and then in a second step after cooling, adding the nanofiller
25 either as a masterbatch/concentrate which has been intercalated with polymer and delaminated/exfoliated and mixing at temperatures of up to about 200°C, or adding the nanofiller(s) to the grafted (co)polymer and intercalating with polymer/delaminating/exfoliating the nanofiller at
30 temperatures of up to about 200°C.

In a further variation of the process of the invention, the (co)polymer, nanofiller and/or other additives are advantageously dry or dried in a separate step prior to processing involving hot air or dessicated
35 hot air, in particular when silane grafting is used.

The composition of the invention can be formed by any suitable known process including moulding, such as

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- injection moulding, blow moulding or compression moulding; pressing; vacuum forming; extrusion such as co extrusion, tandem extrusion or lamination with other layers for example polymeric layers; calendering and heat shrinking.
- 5 The heat shrinking process involves cross-linking the article of the composition and heating and stretching the composition and then cooling the composition in its stretched state. When the heat shrinkable articles are re-heated to temperatures above the crystalline melting
- 10 point, they display shape memory properties, that is, they retain or regain or shrink to their original shape and size.

The composition of the present invention is either cross-linkable in the form of granules, pre-mixes
15 or mixes, pellets, tapes or profile or intermediary, semi-fabricated articles or cross-linked in the form of intermediary, semi-fabricated or final articles. Examples of articles include profiles, tubes, pipes, films, sheet, tiles, floor coverings, containers and packaging for food.

20 The compositions of the present invention possess advantageous properties including high modulus and strength, increased barrier properties such as reduced penetration, permeation and/or lower diffusion of chemical solvents, oils and gases, reduced swelling, high heat
25 distortion temperatures, increased dimensional stability, no melting, improved flame retardancy, lower specific gravity/density. These properties exist and their improvements are more evident in particular at high temperatures or in adverse environmental conditions.

30 Examples of applications of the composition include:

Medical: protective gear and clothing, medicine containers, layered products;

Defence applications and work protection:
35 protection against external chemicals, substances;

Transport: land, vehicles, trains, subways, sea, ships, air, transport of liquids or gases such as

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- pipelines, pipes for hot water under pressure and gas;
- Construction: high rise, towers, installations and rooms with electronics, switches, computers, offices, public areas, theatres, cinemas, malls, stations,
- 5 airports, telecom installations, storage, pipes and tubes;
- Agriculture;
- Food: packaging of consumables, protecting food in laminated films; and
- Packaging: of chemicals, paints, liquids,
- 10 solutions, dispersions, aqueous or solvent based.

EXAMPLES

- The invention will now be described with reference to the following non-limiting examples.
- 15 The compositions of the examples were prepared using various continuous co-rotating twin-screw mixers of ZSK type from Werner & Pfleiderer ZSK and/or Toshiba TEM, of different sizes and build. The compositions of Comparative Examples 1 and 2 and Examples 1 to 3 were
- 20 prepared on a ZSK-53 line A with the co-rotating screws of 53mm diameter each with screw speeds of around about 200 rpm and feeding of about 50 kg/hour. The compositions of Examples 4 to 6 were prepared on a ZSK-120 with co-rotating screws of 123mm diameter with down stream feeders
- 25 (lineD), using a range of around 150 to 180 rpm and a feeding rate of up to about 400 kg/hour.

- The compositions of Examples 9 to 24 were mixed on a ZSK (line A) with 53mm screw diameters (same as for Examples 1 to 3), unless indicated otherwise, namely:
- 30 Examples 7 to 9, 12 to 22 were made on line A. The screw speeds were however in the range of 180 to 200 and in some examples even to 250 rpm as it was found that exfoliation was improved at higher speeds.
- The compositions of Examples 11 and 12, (similar to Examples 4 to 6) were prepared on a TEM 120mm line with screw diameters of 123mm with down stream feeders.
- 35 Various screw speeds and temperature ranges were used,

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adequate to the task and (co)polymer(s) and type of peroxide-silane mixes used in case of grafting or a grafting step. The screw speeds were varied and used up to 250 rpm such as in Example 15.

5 The temperature was in the general range of 180-220°C for LLDPE and 190-240°C for HDPE.

The temperatures were in a number of Examples kept below about 200°C on the extruder zones and 210°C melt temperature at the exit to minimise degradation effects on 10 the and to protect the intercalating agent in the nanofiller; in case of grafting the temperatures were at or around 190°C preferably 200 to 210°C in the extruder zones and 210°C to about 220°C or more at the exit melt temperatures or higher, in particular when the grafting 15 was performed in a second step.

In Comparative Examples 1 and 2 and Examples 1, 2, 5 and 7, the components were mixed and grafted in the first step and either no nanofiller was added or nanofiller was added in the same step (Examples 1 and 2), 20 or later (Example 8). Examples 8 and 9 were made using compositions pre-mixed with nanofillers from Examples 7 and 4 and other PE additives followed by grafting with peroxide and silane in a second step.

In Examples 12, 13 and 14, the components were 25 mixed, grafted and further intercalated with polymer and/or exfoliated in one step, with the addition of some components.

In Examples 3, 4, 6, 10, 11, 15A, 15B, 17, 19A, 20A and 21 the components were mixed with nanofillers and 30 the (co)polymer(s) processing them for further intercalation (with the polymer and/or co-polymer) and for exfoliation in a first step and these compositions were then available for use as such or mixed with additional (co)polymer(s) and with vinylsilane and peroxide for 35 grafting in a second step.

Examples 16, 18, 19B and 22 were prepared using compositions from Examples 15A, 17, 19A and 20

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respectively which were prepared in a separate first step in which the nanofiller was added and further intercalated/exfoliated and then in the second step, grafting with vinylsilane and peroxide and further 5 exfoliation was performed. . .

Example 21 was also made in a second step using the masterbatch composition from example 20 added to additional PE polymers with further exfoliation. Example 10 21 can be used as such and is cross-linkable when grafted with peroxide and siloxane in the same second step or in a separate third step.

Some of the additives and nanofillers were added as pre-mixed or as a master-batch or concentrate. This was also the case in the examples where the compositions 15 from previous examples were used in a second step.

In some of the examples, the nanofiller was mixed with a polar (co)polymer(s) and intercalated/exfoliated in a first step forming a pre-mix or masterbatch or concentrate and then mixed with more or 20 added (co)polymer(s) with silane grafting and further intercalation/exfoliation in a second step.

A nitrogen blanket was used in each example (i.e. the feeding zone or zones were under nitrogen atmosphere for safety reasons and also for more efficient 25 use of the peroxide radical initiator).

The processing was done as far as possible under dry conditions.

The compositions were granulated or pelletised directly at the exit of the ZSK mixers. Packaging was in 30 metal lined bags of various size.

The silane grafted material was mixed with 4% of a catalyst masterbatch of e.g. DLDTP which is an accelerator catalyst directly prior to the formation of a product e.g. extrusion forming to tapes or to injection 35 moulding for test plaques or prior to extrusion or extrusion of larger items or blow forming. These were then cross-linked in hot water, at temperatures of 90 to

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110°C for 1 to 2 up to 4 hours, depending of the thickness of the sample.

- The testing was performed to Australian Standards (AS) which are in general harmonised with 5 International Standards such as IEC, BS, DIN/VDE, EN (European Norms) and to ASTM test methods.

Mechanical properties were tested to above standards.

- Oil resistance (O.R.) was tested to ASTM using 10 ASTM oil nr.2, a criterion is the retention of 70% of original properties.

Environmental stress crack resistance (ESCR) was also tested to ASTM (AS) in tensioactive liquid at 50°C, with unnotched samples. In general, results of over 100 15 hours are aimed to be achieved. In the case of nanocomposites and in particular cross-linked nanocomposites, results of thousands of hours e.g. 8000 hours were achieved and are still ongoing.

- Hot Set test (HST) was made to AS: non-cross-linked materials, including nanocomposites would fail the test at above their melting temperatures and break anyway after short time anyway at 200°C. The requirement for cables is a maximum elongation under load of 175%. After 20 minutes and taking the load away the samples must 25 revert to a maximal residual elongation of 15% or 25% for rubber/ elastomers.

For other applications the requirements are not so restricted.

- The elongations under load could be higher. 30 The cross-linked or cross-linkable compositions of the present invention pass the HST.

Gel content was performed in boiling xylene to ASTM. The gel content shows that a composition has some degree of cross-linking. The main test for cross-linking 35 is the HST. The gel content in silane grafted cross-linked materials is less related to the HST.

Impact resistance is tested to ASTM D-256 Izod

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pendulum impact resistance of notched plastics.

The components used in the examples are from:

Qenos, Melbourne, Australia: for HDPE GM7655,

GA7260H, HD1090, HD6025, LLDPE Alkatuff 425;

5 BASF Ludwigshafen, Germany: for HDPE HMW Lupolen
4261A;

Sabic, LLDPE Ladene MG200024;

DuPont, USA: EVA Elvax 470, Elvax 750, Elvax
760, MAH-HDPE Fusabond MB100D;

10 Sud-Chemie, Moosburg, Germany: Nanofil 15,
Tixogel MP100;

SCP Southern Clay Products, Gonzales, TX, USA:
Cloisite 15A, Cloisite 20A;

15 Crompton, USA/Switzerland: Silox VS 911, Silox
VS294, Peroxide and Silane mix.

Other suppliers of similar materials e.g.

Degussa, Germany, etc. CIBA, Switzerland: Antioxidants,
Stabilisers: Irgafos FF168, Irganox B900;

20 Great Lakes Chemicals, USA: Antioxidants: Anox
20.

Compco Pty Ltd, Melbourne, Australia: Compylene Master-
batches of Antioxidant: EL900140AO, Processing aid:
FL90016PA5.

25 The proportions of the components used in the
compositions of the Examples are given in % by weight of
the total composition. These %s have been rounded to the
first decimal point.

Comparative Example 1

30	HDPE Qenos GM7655 MFI 0.2, granules.....	83.5%
	HDPE Qenos GA7260H MFI 25, powder.....	14.7%
	Silox VS 911 Crompton.....	1.2%
	Stabiliser Irganox 168 FF.....	0.2%
35	Anox 20 Great Lakes.....	0.4%

Hot Set Test (at 200°C):

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Elongation under load.....	37%
Residual elongation relaxed, no load.....	0%

Comparative Example 2

5

LLDPE Alkatuff 425 (MFI 2.5) granules.....	78.7%
LLDPE Ladene MG200024, (MFI 20)powder.....	19.7%
Silox VS 924 (Vinyl silane and Peroxide).....	1.4%
Irganox B 900.....	0.2%

10

Hot Set Test (at 200°C):

with load.....	270%*
without load.....	10%

*requires more Silox addition to 1.6%

15

Example 1

LLDPE Alkatuff 425 granules.....	73.8%
LLDPE Ladene GM200024, powder.....	18.4%
20 Silox VS 924.....	1.6%
MAH-HDPE Fusabond MB 100D.....	1.0%
Irganox B 900.....	0.2%
Tixogel MP 100 Sudchemie.....	5.0%

25

Hot Set Test (at 200°C):

under load.....	77%
without load.....	0%

30

LLDPE Alkatuff 425 granules.....	74%
LLDPE Ladene powder.....	18.5%
Silox VS 924.....	1.4%
MAH-HDPE Fusabond MB 100 D.....	1.0%
35 Antioxidant Irganox B 900.....	0.1%
Tixogel MP 100 filler.....	5.0%

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Hot Set Test (at 200°C) :

under load.....	100%
without load.....	0%

- 5 The addition of Tixogel has significantly improved the cross-linking of the composition compared to Example 2.

Example 3

10 LLDPE Alkatuff 425 granules.....	79.3%
LLDPE Ladene powder.....	14.0%
MAH-HDPE Fusabond MB 100 D.....	1.0%
Irganox 168 FF.....	0.2%
Anox 20.....	0.4%
15 Tixogel MP 100.....	5.1%
Flexural modulus, Mpa.....	557
Tensile Strength (TS), at yield Mpa.....	24.2
Tensile strength at break Mpa.....	13.2
20 Impact resistance Izod, J/m.....	273

This composition is cross-linkable and not grafted nor cross-linked.

Example 4

25 HDPE HMW Lupolen 4261A powder.....	88.1%
Stabiliser mix:	
Irgafos 168FF+Anox20+Ca-Stearate(0.2+0.2+0.5%).....	0.9%
30 MAH-HDPE Fusabond MB 100D.....	1.0%
Tixogel/Lupolen mix (30% Tixogel: 70% Lupolen):	
Lupolen 4261A.....	7.0%
Tixogel MP100 (via side feeder).....	3.0%
35 Flexural modulus, Mpa.....	531
TS at yield Mpa.....	22.1
TS at break Mpa.....	17.3

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Elongation at break.....	568%
Impact resistance Izod, J/m.....	156

This composition is made in one step and is not grafted
 5 nor cross-linked.

Example 5

HDPE GM 7655 granules.....	82.0%
10 Lupolen 4261 powder* (pre-mixed with following Silox)	13.4%
Silox VS 911* (pre-mixed with above Lupolen powder)	1.6%
Processing aid Compylene FL900140AO.....	1.0%
(Masterbatch/concentrate:5% Fluorocarbon polymer in 90% LLDPE) Stabiliser/Antioxidant masterbatch EL900140AO..	2.0%
15 (10% Irganox B900 and 90% LLDPE)	

The Pre-mix* of Lupolen and Silox was high speed
 pre-mixed and added via a separate feeder.

20 Hot Set Test (at 200°C):

Elongation with load.....	160%
Elongation relaxed (after removing load)	7%
Flexural modulus, Mpa.....	558
TS (at yield, Mpa.....	23
25 TS at break, Mpa.....	14.8
Impact resistance Izod, J/m.....	771

Example 6

30 Composition from Example 5 [90%]

HDPE GM 7655 granules*.....	73.0%
HDPE GA 7260H powder*.....	11.9%
Silox VS 911*.....	1.4%
Antioxidant* (masterbatch/concentrate)	1.8%
35 Process aid* (masterbatch/concentrate)	0.9%
MAH-HDPE Fusabond 100 D.....	1.0%
[Subtotal of grafted composition* ex. 5.....	90%

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Composite mix**(incl. Tixogel filler) [10%]

(above 10% comp. mix** consisting of:

Tixogel MP 100(via side feeder).....	3.0%
5 Irgafos 168FF(process stabiliser).....	0.2%
Calcium stearate.....	0.5%
HDPE, MFI 20, MG 20224 powder.....	0.9%
HDPE Lupolen 4261A.....	2.1%
Composition of Example 5.....	3.1%
10 Anox 20.....	0.2%
Subtotal of composite mix**.....	10.0%
Total composition example 6.....	100%

*These components were pre-mixed and grafted separately.

15

Hot Set Test (at 200°C):

elongation under load.....	173%
elongation with load removed (relaxed).....	7%

20 Example 7

HDPE MFI 10, HD1090 granules.....	88.3%
LLDPE Ladene MG200024 powder.....	9.7%
Silox VS 911.....	1.6%
25 Irgafos 168 FF (process stabiliser).....	0.2%
Anox 20.....	0.2%

After grafting and prior to forming, 5% catalyst masterbatch/concentrate was added.

30

Hot Set Test (at 200°C)

Elongation under load.....	250%
Residual elongation relaxed.....	16%

Flexural modulus, Mpa.....	552
TS at yield Mpa.....	24.2
TS at break Mpa.....	15.5

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	Gel content (BS EN579, after boiling in xylene):.....	54.7%
	O.R. (Oil Resistance ASTM Oil nr.2 100°C, 24 hrs):	
	O.R.TS(yield) retained:82.1%;	
5	TS(break) retained:.....	143%
	O.R. EB (elongation at break) change:.....	+133%
	O.R.: change in dimensions:.....	+4%
	Impact resistance Izod, J/m.....	686
	ESCR (ASTM) F0, hours.....	8820
10	(environmental stress crack resistance, at 50°C. No failure after 8820 hours, ongoing)	

Example 8

15	Composition of Example 7.....	86.9%
	HDPE Ladene GM200024 (MFI 20)powder.....	8.7%
	Tixogel MP100.....	3.0%
	Stabiliser mix composed of:	
	Irgafos 168FF (process stabiliser)	0.2%
20	Anox 20 antioxidant.....	0.2%
	MAH-HDPE Fusabond MB100D.....	1.0%

	Hot Set Test (at 200°C):	
	load.....	167%
25	relaxed.....	13%
	TS at yield, Mpa.....	25.6
	TS at break, Mpa.....	16.5
	Flexural modulus, Mpa.....	655
30	Gel content (BS EN 579).....	55.8%
	O.R. (oil resistance ASTM Oil nr.2, 100°C, 24 hrs):	
	O.R. TS(yield) retained: 82.5%; TS(@break)ret.....	131%
	O.R. EB(elong. @ break) change:.....	+105%
35	O.R. change in dimensions.....	3.5%
	Impact resistance Izod, J/m.....	221
	ESCR, F0(no failure, ongoing)hrs.....	8820

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Example 9

	Composition of Example 4.....	88%
	HDPE GM5010T2 powder.....	10%
5	Antioxidant.....	0.4%
	Silox VS 911.....	1.6%
	HST (Hot Set Test 200°C, 200 kPa):.....	63%
10	<u>Example 10</u>	
	HDPE 1090.....	53%
	GM 7655 powder.....	15%
	MAH-HDPE Fusabond MB100D.....	15%
	Nanofil 15 (via side feeder).....	15%
15	Antioxidant EL900140(10% Irganox B900, 90%LLDPE)	2%
	TS at yield, Mpa.....	28.5
	TS at break, Mpa.....	11.6
	Flexural modulus, Mpa.....	912
20	Impact resistance Izod, J/m.....	155

This composition is not-grafted nor cross-linked. It can be silane grafted and cross-linked or added as a masterbatch to other compositions to have a Nanofil concentration of 5 or 3% and to be grafted and cross-linked.

	<u>Example 11</u>	
	HDPE GF 7655.....	83%
30	HDPE GM 7655 powder.....	5%
	MAH-HDPE Fusabond MB100D.....	5%
	Antioxidant EL900140(10% Irganox B900, 90% LLDPE)	2%
	Cloisite 20A* (via side feeder).....	*5%
	Nanofil 15 (via side feeder).....	5%
35	TS at yield, Mpa.....	26.9* 29.2
	TS at break, Mpa.....	11.5 11.5

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Flexural modulus, Mpa.....	757	851
Impact resistance Izod, J/,m.....	161	193

This composition may be grafted and with vinylsilane and
 5 peroxide for subsequent cross-linking. Alternatively, the
 composition may be cross-linked after peroxide addition or
 other cross-linking.

Example 12

10 EVA Elvax 760 (9.3%VA, MFI2= 2).....	83.2	
LLDPE Ladene MG200024 (20MFI) powder.....	10	
Nanofil 15.....	5%	
Silox VS 924.....	1.8%	
15 HST:.....	50%	

Example 13

MAH-HDPE Fusabond MB100D.....	83.2%	
LLDPE Ladene MG200024 (MFI20).....	10%	
20 Nanofil 15.....	5%	
Silox VS 924.....	1.8%	

TS at yield, Mpa.....	25.2	
TS at break, Mpa.....	15.0	
25 Flexural modulus, Mpa.....	654	
O.R. (oil resistance), TS @ break retained:.....	99%	
O.R. EB (elongation @ break) retained.....	95%	
Gel content:.....	28.8%	
Impact resistance Izod, J/m.....	103	

30

Example 14

MAH-HDPE Fusabond MB100D.....	83.2%	
LLDPE Ladene MG200024 (MFI20).....	10%	
Nanofil 15 (dried).....	5%	
35 Silox VS 924.....	1.8%	

TS at yield, Mpa..... 25.0

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	TS at break, Mpa.....	15.2
	Flexural modulus, Mpa.....	636
	Gel content:.....	34%
	O.R. (100°C, 24 hrs), TS @yield retained:.....	80%
5	O.R. " " TS @ break retained:.....	95%
	O.R. (" "), EB retained:.....	90.5%
	Impact resistance Izod, J/m.....	114

Example 15

10	Elvax 750 EVA (9%VA, MFI2= 7).....	70%
	LLDPE Ladene MG200024 (MFI20).....	15%
	Nanofil 15.....	15%

This composition is not grafted nor cross-linked.

15

	<u>Examples:</u>	<u>Ex. 15A</u>	<u>Ex. 15B</u>
	Mixed at rpm:	200 rpm	250 rpm
	HDT(°C)	36	35
	TS at yield, Mpa	8.2	8.3
20	TS at break, Mpa	8.4	8.5
	Elongation at break, %	110	107
	Flexural modulus, Mpa	222	242

[Note: increase in flexural modulus with increase in rpm]

25

	<u>Example 16</u>	
	HDPE Qenos GF 7660.....	54.9%
	LLDPE GME200024 powder.....	10%
	Composition of Example 15A.....	33.3%
30	Silox VS 911.....	1.8%

HST (hot set test at 200°C):..... 23%

	<u>Example 17</u>	
35	EVA Elvax 470(18%VA, MFI2= 0.7).....	70%
	LLDPE Ladene MG200024 (20MFI)powder.....	15%
	Nanofil 15.....	15%

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This composition is not grafted nor cross-linked.

	HDT: °C.....	41
5	TS at yield, Mpa.....	7.9
	TS at break, Mpa.....	12.6
	Elongation at break, %.....	420
	Flexural modulus, Mpa.....	851
10	<u>Example 18</u>	
	HDPE GF 7660.....	54.9%
	LLDPE GM200024 powder.....	10%
	Composition of Example 17.....	33.3%
	Silox VS 911.....	1.8%
15		
	TS at yield, Mpa.....	24.7
	TS at break, Mpa.....	22.0
	HST (at 200°C, 200kPa):.....	20%
	Gel content (BS EN 579, boiling xylene):.....	67.1%
20	O.R.: TS @ break retained:.....	95%
	O.R. EB retained:.....	115%
	Impact resistance Izod, J/m.....	560
25	<u>Example 19</u>	
	<u>Example 19A</u>	
	MAH-HDPE Fusabond MB100D.....	70%
	LLDPE Ladene MG200024 (MFI 20).....	15%
	Tixogel MP100.....	15%
30	The components were mixed in one step. This composition is not grafted nor cross-linked.	
	<u>Example 19B</u>	
35	HDPE Qenos GF 7660.....	54.9%
	LLDPE Ladene GM200024 powder.....	10%
	Composition of Example 19A.....	33.3%

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	Silox VS 911.....	1.8%
	TS at yield, Mpa.....	30.7
	TS at break, Mpa.....	26.0
5	Flexural modulus, Mpa.....	744
	HST: (excellent).....	27%
	Gel content.....	55.3%
	O.R. TS @break retained:.....	104%
	O.R. EB (elong. at break) retained:.....	154%
10	" change.+54%	
	O.R. change in dimensions :- 3% resp. 5%	

Example 20

	MAH-HDPE Fusabond MB100D.....	70%
15	LLDPE Ladene MG200024 (MFI=20).....	15%
	Nanofil 15.....	15%

This composition is not grafted nor cross-linked.

20 Example 21

	HDPE GF7660.....	56.7%
	LLDPE GM200024 powder.....	10%
	Composition of Example 20.....	33.3%

25 This composition is not grafted nor cross-linked.

The Nanofil 15 content after the composition from Example 20 is mixed with the other components is 5%.

	Flexural modulus, Mpa.....	839
30	TS at yield, Mpa.....	27.7
	TS at break, Mpa.....	12.4
	Impact resistance Izod, J/m.....	100

Example 22

	HDPE GF 7660.....	54.9%
	LLDPE GM200024 powder.....	10%
	Composition of Example 20.....	33.3%

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	Silox VS 911.....	1.8%
	HST:.....	40%
5	<u>Example 23</u>	
	EVA Elvax 750 (VA 9%, MFI2=7).....	66.7%
	Composition of Example 15A, granules.....	33.3%
	(mixed granules, by injection moulding)	
	TS at break, Mpa.....	8.2
10	Elongation at break, %.....	140

This composition is not grafted nor cross-linked.

-

	<u>Example 24</u>	
15	EVA Elvax 470 (VA 18%, MFI2=0.7%).....	66.7%
	Composition of Example 17.....	33.3%
	(mixed granules, by injection moulding)	
	TS at break, Mpa.....	10.9
	Elongation at break, %.....	359
20		

This composition is not grafted nor cross-linked.

	<u>Example 25</u>	
	HDPE 1090.....	83%
25	HDPE GM 7655 powder.....	5%
	MAH-HDPE Fusabond MB100D.....	5%
	Nanofil 15.....	5%
	Antioxidant EL-900140.....	2%
30	TS at yield, Mpa.....	29.2
	TS at break, Mpa (inj. moulded dumbells).....	11.2

Many modifications may be made to the preferred embodiment as described above without departing from the spirit and scope of the present invention.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A cross-linkable and/or cross-linked nanofiller composition which comprises a cross-linkable and/or cross-linked ethylene (co)polymer and an intercalated nanofiller.
2. A composition according to claim 1, in which the ethylene (co)polymer is selected from polyethylene and ethylene based alkene or alphaolefin copolymers.
3. A composition according to claim 1 or claim 2, in which the ethylene (co)polymer is high density polyethylene (HDPE), medium density polyethylene (MDPE), linear low density polyethylene (LLDPE), low density polyethylene (LDPE), very low density polyethylene (VLDPE), ultra low density polyethylene (ULDPE), an ethylene hexene copolymer, an ethylene octene copolymer, a butylene (co)polymer, an ethylene-propylene copolymer (EPM), an ethylene-propylene-diene terpolymer (EPDM), an ethylene-butylene copolymer (EBM) or terpolymer (EBDM), an ethylene-vinylsilane (co)polymer, a copolymer or terpolymer of ethylene with acrylic acid (EA) or ethylene with ethylene acrylate and acrylic acid (EAA) or methacrylic acid (EMA) and/or a copolymer of ethylene with ethylacrylate (EEA), butyl-acrylate (EBA) or vinyl acetate (EVA).
4. A composition according to claim 3, in which the butylene (co)polymer is polybutylene or polyisobutylene.
5. A composition according to any one of claims 1 to 4, in which the ethylene (co)polymer is in the form of a metallocene catalyst ethylene (co)polymer.
6. A composition according to any one of claims 1 to 5, in which the ethylene (co)polymer or part thereof is

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grafted with compounds containing carboxylic acid or anhydride group(s).

7. A composition according to claim 6, in which the
5 carboxylic acid or anhydride group is maleic anhydride or
acid or fumaric anhydride or acid.

8. A composition according to claim 6 or claim 7,
in which the grafted ethylene (co)polymer is a maleic
10 anhydride (MAH) or maleic acid grafted copolymer.

9. A composition according to claim 8, in which the
maleic anhydride (MAH) or maleic acid grafted copolymer is
LDPE-MAH, HDPE-MAH, EP-MAH, EPR-MAH, PE-MAH or PP-MAH.

15 10. A composition according to any one of claims 1
to 9, in which the ethylene (co)polymer contains polar
group(s).

20 11. A composition according to claim 10, in which
the polar group(s) are carboxylic group(s), maleic
group(s) and/or ester group(s).

12. A composition according to claim 10 or claim 11,
25 in which the amount of (co)polymer with polar group(s) is
about 0.01% of the total (co)polymer.

13. A composition according to any one of claims 10
to 12, in which the amount of (co)polymer with polar
30 group(s) is about 0.5% of the total (co)polymer.

14. A composition according to any one of claims 10
to 13, in which the amount of (co)polymer with polar
group(s) is at least about 5% of the total (co)polymer.

35 15. A composition according to any one of claims 10
to 14, in which the amount of (co)polymer with polar

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group(s) is at least about 8% of the total (co)polymer.

16. A composition according to claim 3, in which the ethylene content of the ethylene-propylene copolymer is
5 about 10 to about 99.9% by weight.

17. A composition according to claim 3 or claim 16, in which the ethylene content of the ethylene-propylene copolymer is about 40 to about 99.9% by weight.

10 18. A composition according to any one of claims 3, 16 and 17, in which the ethylene content of the ethylene-propylene copolymer is about 75 to about 99.9% by weight.

15 19. A composition according to claim 3, in which the vinyl acetate content of the ethylene-vinyl acetate copolymer (EVA) is about 3 to about 80% by weight.

20 20. A composition according to claim 3 or claim 19, in which the vinyl acetate content of the ethylene-vinyl acetate copolymer (EVA) is about 9 to about 70% by weight.

25 21. A composition according to any one of the preceding claims, in which the ethylene (co)polymer is a plastomer or an elastomer.

22. A composition according to claim 21, in which at least about 40% to about 50% by weight of the total weight of (co)polymer is a plastomer with the balance being an
30 elastomer.

23. A composition according to claim 21 or claim 22, in which at least about 60% by weight is a plastomer with the balance being an elastomer.

35 24. A composition according to any one of claims 21 to 23, in which the plastomer is HDPE, MDPE, LDPE, LLDPE,

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VLDPE, EVA with up to about 30% vinyl acetate, EPM with up to about 25% propylene and/or an ethylene octane copolymer with S.G. up to about 0.886.

5 25. A composition according to any one of claims 21 to 24, in which the elastomer is an ethylene octane copolymer with an S.G. of at least about 0.887, ULDPE, ethylene propylene copolymer, an ethylene vinyl acetate copolymer with greater than about 38% vinyl acetate, EPDM, 10 EPM, and/or EPR.

15 26. A composition according to claim 25, in which the ethylene propylene copolymer is a terpolymer with a propylene co-monomer of greater than about 30%.

20 27. A composition according to claim 35, in which the vinyl acetate content for plastomeric EVA is about 9 to about 30% by weight.

25 28. A composition according to claim 25, in which the vinyl acetate content for elastomeric EVA is about 38 to about 50% by weight.

30 29. A composition according to any one of the preceding claims, in which the cross-linkable and/or cross-linked ethylene (co)polymer forms at least about 40% by weight of the total weight of (co)polymer.

35 30. A composition according to any one of the preceding claims, in which the nanofiller has particle(s) in the order of size of less than 50nm.

31. A composition according to any one of the preceding claims, in which the thickness of the nanofiller particles is about 1nm to about 100nm.

32. A composition according to any one of the

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preceding claims, in which the diameter or length or width of the nanofiller is up to about 500nm.

33. A composition according to any one of the
5 preceding claims, in which the layers of the nanofiller
are composed of silicate.

34. A composition according to any one of the
preceding claims, in which the nanofiller is intercalated
10 with an organic intercalatent.

35. A composition according to claim 34, in which
the organic intercalatent is an ionic or polar
compound(s).

15 36. A composition according to claim 35, in which
the ionic or polar compound(s) is a quaternary ammonium
salt.

20 37. A composition according to claim 36, in which
the quaternary ammonium salt is an optionally substituted
long chain hydrocarbon quaternary ammonium salt.

38. A composition according to claim 37, in which
25 the optionally substituted long chain hydrocarbon
quaternary ammonium salt is a benzyl or alkyl substituted
long chain hydrocarbon quaternary ammonium salt, an alkyl
substituted tallow or hydrogenated tallow quaternary
ammonium salt and/or a bis-hydroxyethyl quaternary
30 ammonium salt.

39. A composition according to any one of claims 36
to 38, in which the counter anion for the quaternary
ammonium cation is a halide or methyl sulphate.

35 40. A composition according to any one of the
preceding claims, in which the nanofiller is an

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intercalated mineral nanofiller or clay which is either synthetic or natural and has been intercalated by organic modification with ionic or polar substances.

5 41. A composition according to claim 40, in which the mineral or clay is montmorillonite, bentonite, smectite and/or phyllosilicate.

42. A composition according to claim 40 or claim 41,
10 in which the nanofiller is Cloisite, Nanofil, Tixogel or Kunipia.

43. A composition according to any one of the preceding claims, in which the amount of nanofiller is
15 about 0.1 to about 15% by weight.

44. A composition according to claim 43, in which the amount of nanofiller is about 1 to about 10% by weight.

20

45. A composition according to claim 43 or claim 44; in which the amount of nanofiller is about 2 to about 6% by weight.

25 46. A composition according to any one of claims 35 to 45, in which the amount of organic intercalatent is up to about 40% by weight of the nanofiller.

47. A composition according to any one of the preceding claims, which further comprises another filler.

48. A composition according to claim 47, in which the filler is an inorganic and/or mineral filler.

35 49. A composition according to claim 47 or claim 48, in which the filler is an optionally calcined clay, talc, mica, kaolin, alkaline earth metal carbonate, and/or metal

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hydroxide.

50. A composition according to claim 49, in which
the alkaline earth metal carbonate is calcium carbonate,
5 magnesium calcium carbonate and/or hydrated basic
magnesium carbonate.

51. A composition according to claim 49, in which
the metal hydroxide is aluminum and/or magnesium
10 hydroxide.

52. A composition according to any one of claims 47
to 51, in which the filler is coated.

15 53. A composition according to claim 52, in which
the filler is coated with stearic acid, stearate, silane,
siloxane and/or titanate.

20 54. A composition according to any one of the
preceding claims, which further comprises an organic
silane grafted to the ethylene (co)polymer and/or
intercalated into the nanofiller.

25 55. A composition according to claim 54, in which
the organic silane is a vinyl silane and/or a long
aliphatic hydrocarbon chain silane.

30 56. A composition according to claim 55, in which
the vinyl silane is a vinyl alkoxy silane.

35 57. A composition according to claim 56, in which
the vinyl alkoxy silane is vinyl-tris-methoxy-silane
(VTMOS), vinyl-tris-methoxy-ethoxy-silane(VTMEOS), vinyl-
tris-ethoxy-silane, vinyl-methyl-dimethoxy-silane and/or
gama-methacryl-oxypropyl-tris-methoxy-silane.

58. A composition according to any one of claims 55

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to 57, in which the vinyl silane is added in an amount from about 0.5 to about 2% by weight.

59. A composition according to claim 58, in which
5 the vinyl silane is added in an amount of about 0.8 to about 2.0% by weight.

60. A composition according to claim 58 or claim 59,
in which the vinyl silane is added in an amount of about
10 1% to about 1.8% by weight.

61. A composition according to any one of claims 54
to 60, in which the organic silane is grafted using a free
radical initiator.

15

62. A composition according to claim 61, in which
the free radical initiator is a peroxide.

63. A composition according to claim 62, in which
20 the peroxide is dicumyl peroxide, di-tertiary-butyl
peroxide, di-tertiary-butyl-cumyl peroxide and/or bis-
tertiary-butyl-cumyl peroxide.

64. A composition according to any one of claims 61
25 to 63, in which the free radical initiator is added in an
amount of about 0.05 to about 0.3% by weight.

65. A composition according to any one of claims 61
to 64, in which the free radical initiator is added in an
30 amount of about 0.15 to about 0.2% by weight.

66. A composition according to any one of the
preceding claims, in which the composition and/or ethylene
(co)polymer are silane cross-linked, cross-linked by
35 adding a cross-linking catalyst or radiation cross-linked.

67. A composition according to any one of the

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preceding claims, which further comprises one or more additives known in the art of polymer processing.

68. A composition according to claim 67, in which
5 the additive is an antioxidant, metal deactivator, copper inhibitor, UV absorber, foaming or blowing agent which is either endothermic or exothermic, processing and/or thermal stabiliser, pigment, flame retardant, extender, plasticiser and/or softener.

10

69. A process for preparing a cross-linkable and/or cross-linked nanofiller composition which comprises either:

(a) mixing and delaminating and/or exfoliating
15 in one step a cross-linkable and/or cross-linked ethylene (co)polymer and an intercalated nanofiller;
(b) mixing a cross-linkable ethylene (co)polymer with an intercalated nanofiller; and
delaminating and/or exfoliating at least
20 part of the nanofiller; or
(c) delaminating and/or exfoliating at least part of an intercalated nanofiller; and
mixing the delaminated and/or exfoliated
intercalated nanofiller with a cross-linkable and/or
25 cross-linked ethylene (co)polymer.

70. A process according to claim 69, in which the ethylene (co)polymer and/or nanofiller are subjected to grafting either before, during or after the mixing and/or
30 exfoliating and/or delaminating step(s).

71. A process according to claim 70, in which the grafting involves treating the ethylene (co)polymer and/or nanofiller with an organic silane which is then grafted
35 onto the (co)polymer and/or intercalated into the nanofiller.

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72. A process according to claim 71, in which the organic silane is grafted using a free radical initiator.

73. A process according to any one of claims 69 to 5 72, which further comprises the step of cross-linking the (co)polymer before step (a) or cross-linking the composition after step (b) or (c).

74. A process according to claim 73, in which the 10 composition and/or ethylene (co)polymer is silane cross-linked, cross-linked by adding a cross-linking catalyst, silane cross-linked or radiation cross-linked.

75. A process according to any one of claims 69 to 15 74, in which the (co)polymer is granulated, pelletised, powderised, cut and/or diced.

76. A process according to any one of claims 69 to 20 75, in which the (co)polymer and the nanofiller are pre-mixed or added simultaneously, sequentially and/or separately to a mixing apparatus.

77. A process according to any one of claims 69 to 25 76, in which the nanofiller or composition are exfoliated and/or delaminated using high shear processing.

78. A process according to any one of claims 69 to 30 77, in which a further exfoliation and/or delamination step is performed at any stage of the process.

79. A process according to any one of claims 69 to 35 78, in which other fillers and/or additives are added simultaneously, sequentially and/or separately at any step of the process.

80. A process according to claim 79, in which the (co)polymer, nanofiller, other fillers and/or additives

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are dry or dried in a separate step prior to step (a).

81. An article which is wholly or partly composed of
the nanofiller composition defined in any one of claims 1
5 to 68.

82. An article according to claim 81, which is a
profile, tube, pipe, film, sheet, tile, floor covering,
container or packaging for food.

10

83. A process for preparing the article defined in
claim 81 or claim 82, which comprises either:

(a) forming or shaping the nanofiller
composition defined in any one of claims 1 to 68; or

15

(b) combining at least one layer of the
nanofiller composition defined in any one of claims 1 to
68 with at least one other layer;

(c) cross-linking the nanofiller composition
defined in any one of claims 1 to 68; or

20

(d) heating and stretching the nanofiller
composition defined in any one of claims 1 to 68 and
cooling the stretched composition.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU03/00385

A. CLASSIFICATION OF SUBJECT MATTERInt. Cl. ⁷: C08K 3/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
IPC: C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT: nanofiller or nanocomposite or intercalat or exfoliat

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/96467 A2 (BASELL TECHNOLOGY COMPANY) 20 December 2001 Whole document.	1-83
X	WO 01/87596 A1 (PECHINEY EMBALLAGE FLEXIBLE EUROPE) 22 November 2001 Whole document.	1-83
X	WO 01/87566 A1 (PECHINEY EMBALLAGE FLEXIBLE EUROPE) 22 November 2001 Whole document.	1-83

 Further documents are listed in the continuation of Box C See patent family annex

* Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be of particular relevance
"B"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search
8 July 2003

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No. PCT/AU03/00385

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	WO 01/66627 A1 (OMNOVA SOLUTIONS INC.) 13 September 2001 Whole document.	1-83
X	WO 01/10948 A1 (EASTMAN CHEMICAL COMPANY) 15 February 2001 Whole document.	1-83
X	EP 1055706 A1 (RHEOX, INC.) 29 November 2000 Whole document.	1-83
X	WO 99/47598 A1 (THE DOW CHEMICAL COMPANY) 23 September 1999 Whole document.	1-83
X	US 5952093 A (Nichols et al.) 14 September 1999 Whole document.	1-83
X	US 5910523 A (Hudson) 8 June 1999 Whole document.	1-83
X	US 5717000 A (Karande et al.) 10 February 1998 Whole document	1-83

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU03/00385

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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WO	01/87596	AU	200159724	BR	200111152	EP	1286831
		US	6447860				
WO	01/87566	AU	200159687	EP	1286810	US	6403231
US	2001/0033924						
WO	01/66627	EP	1268630	US	6414070		
WO	01/10948	AU	200065302	EP	1212373		
EP	1055706	JP	2001019854	US	6521690		
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US	5952093	-					
US	5910523	-					
US	5717000	AU	21322/97	BR	9707867	CA	2247194
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END OF ANNEX